

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 675 971 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:

29.04.1998 Bulletin 1998/18

(21) Application number: **94905314.4**

(22) Date of filing: **09.11.1993**

(51) Int Cl.⁶: **C22F 1/18**

(86) International application number:
PCT/US93/10774

(87) International publication number:
WO 94/14995 (07.07.1994 Gazette 1994/15)

(54) **HEAT TREATMENT TO REDUCE EMBRITTLEMENT OF TITANIUM ALLOYS**

WÄRMEBEHANDLUNG GEGEN VERSPRÖDUNG VON TITAN-LEGIERUNGEN

TRAITEMENT THERMIQUE PERMETTANT DE REDUIRE LA FRAGILISATION D'ALLIAGES DE TITANE

(84) Designated Contracting States:
DE FR GB

(30) Priority: **23.12.1992 US 996211**

(43) Date of publication of application:
11.10.1995 Bulletin 1995/41

(73) Proprietor: **UNITED TECHNOLOGIES
CORPORATION**
Hartford, CT 06101 (US)

(72) Inventors:
• **HANSEN, James O.**
Hobe Sound, FL 33455 (US)

• **NOVOTNAK, David**
Juplter, FL 33458 (US)

(74) Representative: **Schmitz, Jean-Marie et al**
Dennemeyer & Associates Sàrl
P.O. Box 1502
1015 Luxembourg (LU)

(56) References cited:
DE-A- 3 720 111 **FR-A- 1 484 440**
GB-A- 2 148 940 **US-A- 2 974 076**

• **M.J. DONACHIE, JR. 'TITANIUM - A TECHNICAL
GUIDE' 1988, AMERICAN SOCIETY FOR
METALS, METALS PARK, OHIO, US see page 28**
- page 31 see page 57 - page 68

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 0 675 971 B1

Description

The present invention relates to the heat treatment of titanium alloys, and more specifically to a heat treatment of non-burning Ti-V-Cr alloys which permits an increase in the operating temperature without embrittlement of the alloy.

Pure titanium exists in the alpha crystalline form at room temperature, but transforms to the beta crystalline form at 883°C (1621°F). Various alloying elements increase the stability of the beta phase at lower temperatures. Certain known titanium alloys contain sufficient amounts of the beta phase stabilizers that they are largely beta phase under most temperature conditions and are referred to as beta titanium alloys. The subject of these prior "beta" titanium alloys is discussed in "The Beta Titanium Alloys," by F. H. Froes et al., *Journal of Metals*, 1985, pp. 28, 37.

Titanium alloys possess an ideal combination of strength and low density for many aerospace applications, including gas turbine engines, and particularly gas turbine engine compressor blades, vanes and related hardware. However, titanium is a highly reactive metal and can undergo sustained combustion under conditions encountered in gas turbine engine compressors. In such compressors, ambient air is compressed at temperatures on the order of 454°C (850°F) to pressures which may be on the order of 2.75 MPa (400 psi). The air can flow at 137 m/sec (450 feet per second) as it passes through the compressor. Under these conditions common commercial titanium alloys will burn uncontrollably if ignited. Ignition can occur by friction arising from the ingestion of foreign objects or as a result of mechanical failures which cause contact between moving blades and stationary objects, at least one of which is made of titanium alloy, with friction between two titanium components being particularly troublesome. Such combustion is a great concern to gas turbine engine designers who have gone to great lengths to guard against rubbing between titanium components.

The DE-A-3720111 describes a class of true beta titanium alloys based on compositions of titanium-vanadium-chromium which occur in the titanium-vanadium-chromium phase diagram bounded by the points Ti-22V-36Cr, Ti-40V-13Cr and Ti-22V-13Cr (all percentages herein being weight percent unless otherwise noted) has been shown to possess a high degree of resistance to burning (referred to hereinafter as non-burning) under the operating conditions in a gas turbine engine. These alloys also exhibit creep strengths which are greater than those exhibited by the strongest commercial alloys (i.e., Ti-6-2-4-2) at elevated temperatures. A variety of quaternary (and higher) alloying elements may be added to the basic composition to modify the alloy properties.

A particular titanium base alloy, having a nominal composition of 35% V, 15% Cr, balance Ti, has been historically used for gas turbine applications in the fully solutioned (all beta) condition. When operating above 454°C (850°F) for extended periods of time, alpha phase precipitates as an essentially continuous film in the grain boundaries and embrittles the alloy, thus shortening its useful lifetime.

What is needed is a non-burning titanium alloy which can operate for extended periods of time at elevated temperatures without becoming embrittled.

What is further needed is a method of heat treating a non-burning titanium alloy so as to render it resistant to the embrittling effects of long term exposure at elevated temperatures. The method for improving the embrittlement resistance of the non burning titanium base alloy having a nominal composition bounded by the points Ti-22V-36Cr, Ti-40V-13Cr and Ti-22V-13Cr in the Ti-V-Cr ternary system is described in claim 1.

The non-embrittling material of the present invention comprises a non-burning titanium-vanadium-chromium alloy with a composition defined by the region designated in Figure 1 whereby the alloy is heat treated to render it resistant to precipitation of detrimental particles under normal gas turbine engine operating conditions.

The process of the present invention comprises an initial step of heating the material above the alpha solvus temperature for a time sufficient to produce an all beta structure, followed by heat treating below the alpha solvus temperature to produce a precipitate consisting of coarse, stable alpha phase particles generally situated in the grain boundaries.

The initial heat treat step consists of holding the material at 28°C (50°F) above the alpha solvus temperature for from one to ten hours, with one hour generally preferred.

The sub-alpha solvus temperature heat treatment may be either isothermal or ramped. The isothermal heat treatment is conducted at a temperature about 83°C (150°F) below the solvus temperature for two hours, and produces a coarse, stable precipitate of alpha phase, which is a form of TiO₂.

The most preferred ramp heat treatment generally consists of holding at a first temperature below the alpha solvus for a period of time, cooling at a fairly slow rate to a second, lower temperature, holding for a period of time at the second temperature, cooling to a still lower third temperature, holding for a period of time at the third temperature, and cooling to room temperature. The ramp heat treatment initially produces a coarse precipitate of alpha phase, which is further coarsened during the ramp and hold portions of the cycle.

While the preferred ramp heat treatment uses three successively lower sub-solvus holding temperatures, the invention process can also be carried out effectively with more or fewer holding periods, or with a ramp from a first sub-solvus temperature down to a second lower temperature without any intermediate holding periods. While longer total exposure times in the 538-704°C (1000-1300°F) temperature range would tend to improve the properties of the material, an optimum cycle must also consider the overall cost of the operation.

These, and other features and advantages of the invention, will be apparent from the description of the Best Mode, read in conjunction with the drawings.

Figure 1 is an isothermal section of the Ti-V-Cr phase diagram showing the general composition region of the non-burning alloys of this invention.

Figure 2 is a photomicrograph showing the microstructure of PWA 1274 in the as-solutioned condition.

Figure 3 is a photomicrograph showing the as solutioned PWA 1274 material after 500 hours at 538°C (1000°F) in air.

Figure 4 is a photomicrograph of PWA 1274 processed according to the invention.

Figure 5 is a graph showing the results of room temperature elongation testing of PWA 1274 after various heat treat cycles according to the invention process followed by exposure at 538°C (1000°F) for 0-500 hours.

The titanium base alloy used in the heat treatment according to the present invention and containing 35% V, 15% Cr, which lies within the composition ranges of a non-burning alloy as illustrated in Figure 1, and which is hereinafter referred to as PWA 1274, has been shown to be highly burn-resistant in gas turbine engine compressor applications. It is commonly used in the solutioned condition, and has a microstructure as shown in Figure 2. The solutioning process is performed at about 816°C (1500°F), approximately 28°C (50°F) above the alpha solvus temperature of 788°C (1450°F), for about one hour.

While operating above 454°C (850°F) for extended periods of time, the precipitation of alpha phase as a film in the grain boundaries decreases the ductility of the alloy drastically. As measured at room temperature, the elongation of fully solutioned material decreases from an initial value of 20% to 2% after exposure in air at 538°C (1000°F) for 500 hours. The effect of this extended exposure on the microstructure of the alloy is shown in Figure 3.

By heat treating the solutioned, essentially all beta phase, material below the alpha solvus temperature, but at a temperature higher than the normal use temperature, the alpha phase, which is a form of TiO₂, is caused to precipitate in the grain boundaries as coarse, stable particles. These alpha particles are much less harmful to the material than the grain boundary films discussed above. Figure 4 shows a typical microstructure of this heat treated material.

The heat treat cycle of the invention requires that the material be in the fully solutioned condition. The isothermal sub-solvus treatment involves heating the material at a temperature about 83°C (150°F) below the alpha solvus temperature. The solvus temperature is strongly dependent on the oxygen content of the material, so the solvus temperature must generally be determined in order to establish the heat treat temperature for the sub-solvus step. The time required is between one-half and ten hours, with about two hours being generally preferred. The cooling rate from the sub-solvus treatment temperature to room temperature should be at least 56°C (100°F) per hour to avoid grain boundary precipitation.

The most preferred embodiment of the ramp heat treatment process includes heating isothermally at a temperature 83°C (150°F) below the solvus temperature for a period of about one to ten hours, with the preferred time being about two hours, cooling at a rate of 14-56°C (25-100°F) per hour, with a preferred rate of 42°C (75°F) per hour, to a temperature 55°C (100°F) below the first temperature, holding at the second temperature for a period of one to ten hours, preferably six hours, cooling to a third temperature 111°C (200°F) below the second temperature and holding for a period of one to ten hours, preferably six hours, and cooling to room temperature.

Figure 5 is a graph showing the results of ductility testing of PWA 1274 which has been sub-solvus heat treated using various heat treat cycles according to the present invention. The sub-solvus heat treat cycles applied to the solutioned material are indicated in Table I.

Table I

A	704°C (1300°F)/2hr, cool at 42°C (75°F)/hr to 649°C (1200°F)/6hr, cool at 42°C (75°F)/hr to 538°C (1000°F)/6hr, cool at > 56°C (100°F)/hr to room temperature.
B	704°C (1300°F)/2hr, cool at 14°C (25°F)/hr to 566°C (1050°F)/1hr, cool at > 56°C (100°F)/hr to room temp.
C	704°C (1300°F)/2hr, cool at 14°C (25°F)/hr to 621°C (1150°F)/1hr, cool at > 56°C (100°F)/hr to room temp.
D	704°C (1300°F)/hr, cool at > 56°C (100°F)/hr to room temperature.
E	549°C (1200°F)/2hr, cool at > 56°C (100°F)/hr to room temperature.
F	As solutioned (816°C or 1500°F for one hour).

In all cases the heat treated material showed improved ductility compared to the solutioned material. Even with no exposure time at 538°C (1000°F), the heat treated samples had better ductility than the solutioned material. This is attributed to the fact that oxygen dissolved in the beta phase is caused to migrate to the grain boundaries during the heat treat cycle, where it precipitates as alpha phase, or TiO₂, particles. The decrease in dissolved oxygen content in the beta phase increases the ductility of the alloy.

While the measured ductility of the solution heat treated material decreased to about 2% after 500 hours at 538°C (1000°F), the ductility for the sub-solvus isothermally heat treated materials decreased to about 5% after the same

exposure. This indicates that the benefits attributed to controlled removal of dissolved oxygen from the beta phase are significant.

The application of a ramp heat treat cycle to solution heat treated material prior to exposure to elevated temperatures improved the ductility to an even greater extent. The additional time attributed to the ramp cycle and the second holding period apparently allowed a greater portion of the dissolved oxygen to migrate to the grain boundaries.

The ramp treatment to 621°C (1150°F) results in an elongation of about 8.5% after 500 hours at 538°C (1000°F) which is a significant improvement over the elongation after exposure of the isothermally heat treated material to the same conditions. The ramp treatment to 566°C (1050°F) results in an elongation of about 11.5% after the same elevated temperature exposure, which is an improvement of about 30% over the elongation of the 621°C (1150°F) ramp heat treated material. This improvement is attributed to the additional time at the heat treat temperatures, since four more hours were required in the ramp portion of the cycle to cool down to 566°C (1050°F) (at 14°C or 25°F per hour) than were required to cool to 621°C (1150°F).

The three-step ramp heat treatment involved holding at 704°C (1300°F) for two hours, cooling at 42°C (75°F) to 649°C (1200°F), holding for six hours, cooling at 42°C (75°F) to 538°C (1000°F), holding for six hours and cooling to room temperature. As shown in Figure 5, the elongation of this material was about 15% after 500 hours at 538°C (1000°F), which is an improvement over the two-step process. The greater exposure of the material to the elevated temperatures of the heat treat cycles during the three-step process seems to account for the increase in measured ductility.

Claims

1. A method for improving the embrittlement resistance of a non-burning titanium base alloy having a nominal composition bounded by the points Ti-22V-36Cr, Ti-40V-13Cr and Ti-22V-36Cr in the Ti-V-Cr ternary system, comprising:
 - a. heat treating above the alpha solvus temperature for a time sufficient to fully solution the alpha phase; and
 - b. heat treating below the alpha solvus temperature to precipitate coarse alpha particles at the grain boundaries.
2. The method as recited in claim 1 wherein the sub-solvus heat treat cycle consists of holding at a constant temperature for a period of one to ten hours.
3. The method as recited in claim 1 wherein the sub-solvus heat treat cycle consists of holding at a constant temperature for about two hours.
4. The method as recited in claim 1 wherein the sub-solvus heat treatment consists of holding at a first temperature, ramping at a controlled rate to a second temperature lower than the first temperature, holding at a second temperature, and cooling to room temperature at any convenient rate.
5. The method as recited in claim 3 wherein the cooling rate for the ramp cycle is between 6°C (10°F) and 28°C (50°F) per hour.
6. The method as recited in claim 4 wherein the cooling rate for the ramp cycle is 42°C (75°F) per hour.
7. The method as recited in claim 4 wherein the holding period at the first temperature is between one and ten hours.
8. The method as recited in claim 4 wherein the holding period at the first temperature is two hours.
9. The method as recited in claim 4 wherein the holding period at the second temperature is between one and ten hours.
10. The method as recited in claim 4 wherein the holding period at the second temperature is two hours.
11. A non-burning titanium base alloy occurring in the Ti-V-Cr ternary system, having a nominal composition bounded by the points Ti-22V-36Cr, Ti-40V-13Cr and Ti-22V-13Cr, which has been rendered non-embrittling according to the process of claim 1-10.

Patentansprüche

1. Verfahren zum Verbessern der Versprödungsfestigkeit einer unbrennbaren Titanlegierung, die eine nominelle Zusammensetzung hat, welche durch die Punkte Ti-22V-36Cr, Ti-40V-13Cr und Ti-22V-36Cr in dem ternären Ti-V-Cr-System begrenzt wird, durch:
 - a. Wärmebehandeln oberhalb der alpha-Löslichkeitstemperatur für eine Zeit, die ausreicht, um die alpha-Phase vollständig zu lösen; und
 - b. Wärmebehandeln unterhalb der alpha-Löslichkeitstemperatur, um grobe alpha-Partikeln an den Korngrenzen abzuscheiden.
2. Verfahren nach Anspruch 1, wobei der Wärmebehandlungszyklus bei einer Temperatur unterhalb der Löslichkeitstemperatur aus Halten bei einer konstanten Temperatur für eine Zeitspanne von einer Stunde bis zehn Stunden besteht.
3. Verfahren nach Anspruch 1, wobei der Wärmebehandlungszyklus bei einer Temperatur unterhalb der Löslichkeitstemperatur aus Halten auf einer konstanten Temperatur für etwa zwei Stunden besteht.
4. Verfahren nach Anspruch 1, wobei die Wärmebehandlung bei einer Temperatur unterhalb der Löslichkeitstemperatur aus Halten auf einer ersten Temperatur, rampenförmigem Übergehen mit einer gesteuerten Geschwindigkeit auf eine zweite Temperatur, die niedriger als die erste Temperatur ist, Halten auf einer zweiten Temperatur und Abkühlen auf Raumtemperatur mit irgendeiner zweckmäßigen Geschwindigkeit besteht.
5. Verfahren nach Anspruch 3, wobei die Abkühlgeschwindigkeit für den Rampenzyklus zwischen 6 °C (10 °F) und 28 °C (50 °F) pro Stunde liegt.
6. Verfahren nach Anspruch 4, wobei die Abkühlgeschwindigkeit für den Rampenzyklus 42 °C (75 °F) pro Stunde beträgt.
7. Verfahren nach Anspruch 4, wobei die Haltezeitspanne auf der ersten Temperatur zwischen einer Stunde und zehn Stunden beträgt.
8. Verfahren nach Anspruch 4, wobei die Haltezeitspanne auf der ersten Temperatur zwei Stunden beträgt.
9. Verfahren nach Anspruch 4, wobei die Haltezeitspanne auf der zweiten Temperatur zwischen einer Stunde und zehn Stunden beträgt.
10. Verfahren nach Anspruch 4, wobei die Haltezeitspanne auf der zweiten Temperatur zwei Stunden beträgt.
11. Unbrennbare Titanlegierung, die in dem ternären Ti-V-Cr-System vorkommt, mit einer nominellen Zusammensetzung, welche durch die Punkte Ti-22V-36Cr, Ti-40V-13Cr und Ti-22V-13Cr begrenzt wird, welche gemäß dem Verfahren nach Anspruch 1-10 nichtversprödend gemacht worden ist.

Revendications

1. Une méthode pour améliorer la résistance à la fragilisation d'un alliage à base de titane non combustible ayant une composition nominale liée par les points Ti-22V-36Cr, Ti-40V-13Cr et Ti-22V-36Cr dans le système ternaire Ti-V-Cr, comprenant:
 - a. traiter thermiquement au-delà de la température de dissolution de mise en solution de la phase alpha pendant une période de temps suffisante pour mettre entièrement en solution solide la phase alpha; et
 - b. traiter thermiquement en-dessous de la température de dissolution de la phase alpha pour précipiter de gros grains de phase alpha aux limites de grains.
2. Méthode selon la revendication 1 où le cycle de traitement thermique en-dessous de la température de dissolution consiste à maintenir à température constante durant une période de une à dix heures.

3. Méthode selon la revendication 1 où le cycle de traitement thermique en-dessous de la température de dissolution consiste à maintenir à température constante durant environ deux heures.
- 5 4. Méthode selon la revendication 1 où le traitement thermique en-dessous de la température de dissolution consiste à maintenir à une première température, descendre à vitesse contrôlée jusqu'à une seconde température inférieure à la première température, maintenir à une seconde température, et refroidir jusqu'à température ambiante à toute vitesse adéquate.
- 10 5. Méthode selon la revendication 3 où la vitesse de refroidissement pour le cycle progressif est entre 6°C (10°F) et 28°C (50°F) par heure.
6. Méthode selon la revendication 4 où la vitesse de refroidissement pour le cycle progressif est 42°C (75°F) par heure.
- 15 7. Méthode selon la revendication 4 où la période de maintien à une première température est entre une et dix heures.
8. Méthode selon la revendication 4 où la période de maintien à la première température est de deux heures.
9. Méthode selon la revendication 4 où la période de maintien à une seconde température est entre une et dix heures.
- 20 10. Méthode selon la revendication 4 où la période de maintien à la seconde température est deux heures.
11. Un alliage à base de titane non combustible se trouvant dans le système ternaire Ti-V-Cr, ayant une composition nominale liée par les points Ti-22V-36Cr, Ti-40V-13Cr et Ti-22V-13Cr, qui a été rendu non cassant selon le procédé des revendications 1 à 10.
- 25

30

35

40

45

50

55

fig. 1

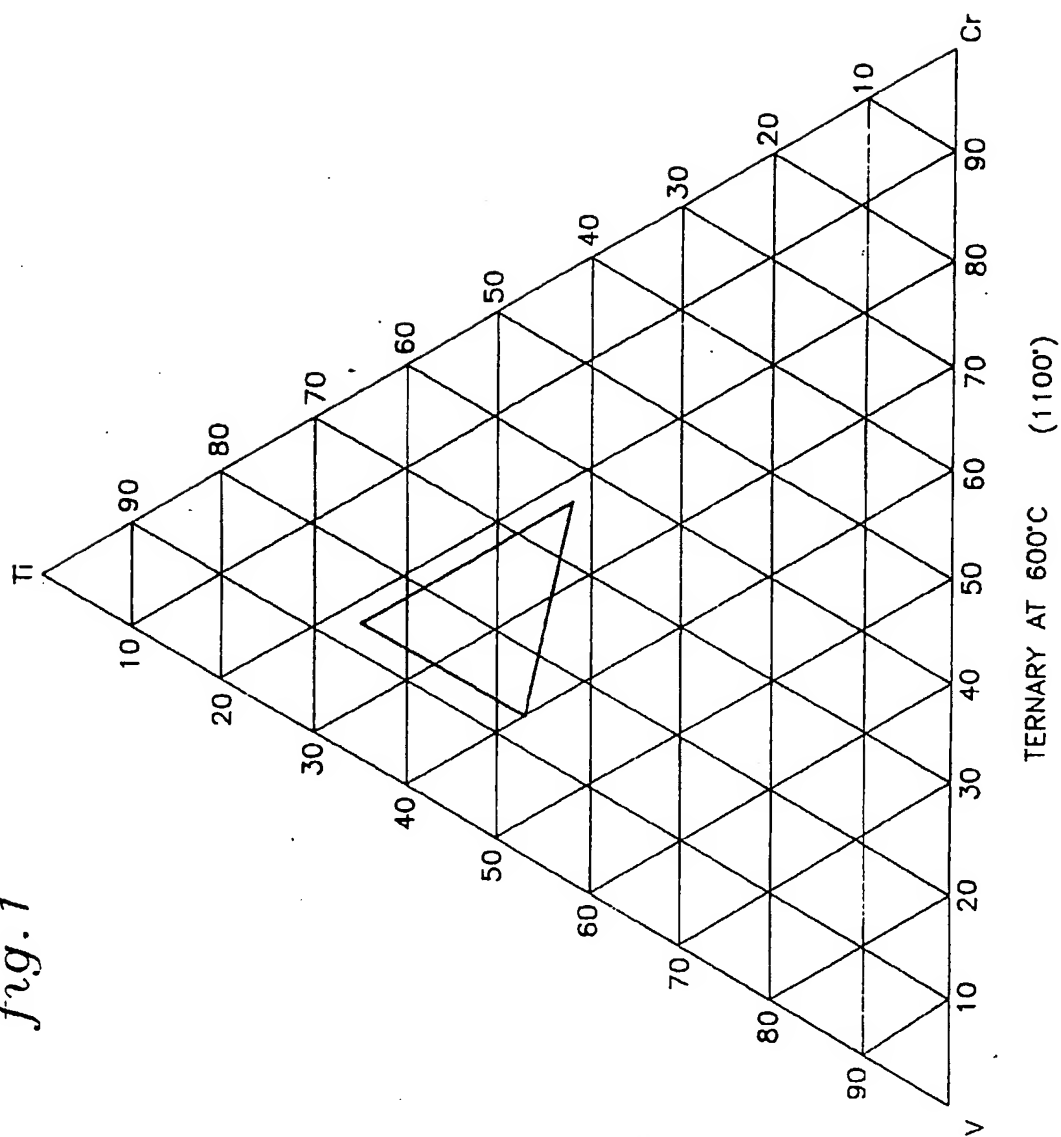


fig.2

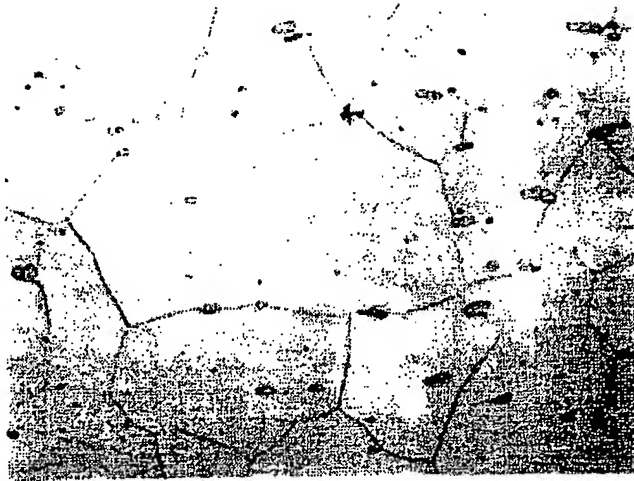


fig.3



fig.4



fig. 5

